



## Measuring Water Vapor Flux Across Model Proton Exchange Membranes

Dan Burnett and Armando R. Garcia, Surface Measurement Systems Ltd.

***Water content and flux are important properties for proton exchange membrane fuel cell performance. This application note describes the use of a novel cell to measure vapour flux or permeation rates across polymer films. Nafion® membranes were used as model membranes. Water vapour flux measurements were performed at three temperatures for three Nafion® membranes.***

### Introduction

Proton Exchange Membrane Fuel Cells (PEMFC) continue to be a robust area of research for use as low pollution power generators for mobile and stationary applications. Water management for both hydrogen based fuel cells and direct methanol fuel cells (DMFCs) is paramount to optimal fuel cell performance and longevity. For instance, the level of hydration within the proton exchange membrane is vital to its performance. If the hydration level is too low, the polymers exhibit greatly reduced ionic conductivity [1], but if hydration is too high, excess water can flood the pores in the gas diffusion layer and block off reaction sites or impede mass transport within the electrode structure [2,3]. In addition, the water vapor diffusion coefficients as a function of water content are important parameters in characterizing the performance of proton exchange membranes [3]. Measuring water flux across PEMFC membranes is important as it can be related to three water transport mechanisms: diffusion due to concentration gradient across the membrane, electro-osmotic drag due to protons dragging water molecules on their way from the anode to the cathode, and hydraulic permeation

due to any pressure difference between the anode and the cathode. Further, for DMFC water management is crucial for removing water from the cathode (reduce flooding) and supplying water to the anode [4]. Additionally, for DMFCs low water flux through the membrane is advantageous as the anode doesn't require large amounts of water and the cathode is less prone to flooding [4].

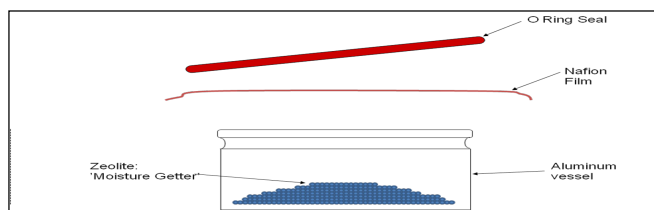
In this study, the water flux across three different Nafion® based membranes was measured over a range of temperatures at 90% relative humidity (RH). Nafion® is an ideal choice for PEMFC applications due to its high chemical and electrochemical stability, sufficient mechanical strength, low permeability to reactant species, selective and high ionic conductivity, and electronic insulation properties [5].

### Method

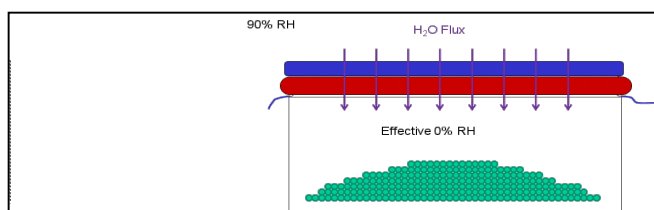
The DVS-Advantage instrument (Surface Measurement Systems, London, UK) used for these studies measures the uptake and loss of vapor gravimetrically using a recording ultra-microbalance with a mass resolution of  $\pm 0.1 \mu\text{g}$ . The vapor partial pressure around the sample is controlled by mixing saturated and dry carrier gas



streams using electronic mass flow controllers. The temperature is maintained constant  $\pm 0.1$  °C, by using the entire system in a temperature-controlled enclosure. A specially designed flux cell was used for these experiments (See Figure 1). This cell consists of a cylindrical aluminum pan and an o-ring. A film ( $\sim 1\text{cm}^2$ ) is stretched over the pan and sealed with the o-ring. For the flux experiments the pan was filled with a zeolite powder, which acts as a moisture scavenger. This creates an effective 0% RH inside the pan and the back side of the film. The pan is then placed in the instrument at the desired temperature and 0% RH to establish a dry mass. Finally, the relative humidity was set to 90% RH and the mass change was recorded as a function of time. Any mass increase recorded by the ultrabalance would be due to water uptake by the film and water flux across the film (sorbed by zeolite). Water sorption by the pan or o-ring is negligible. Identical experiments were performed using the film without any zeolite in the pan, which measures water uptake by the film only. The experiment using the film only was then subtracted from the film plus zeolite experiment to isolate mass gain due to water flux across the film only. Flux experiments were measured at 25, 40, and 60 °C.



(a.)



(b.)

Figure 1. Schematic of flux cell used for these experiments in exploded view (a.) and assembled view (b.).

Three different Nafion® films were obtained from DuPont: N-117, N-112, and NR-112. N-117 and N-112 are non-reinforced extruded films while the

NR-112 sample is a non-reinforced dispersion-cast film. The N-117 sample is 183 microns thick at 23 °C and 50% RH, while the N-112 and NR-112 samples are 51 microns thick at the same conditions.

## Results

Figure 2 shows the moisture flux results for the NR-112 sample at 25 °C. The solid trace displays the change in mass for the film sample with the zeolite, versus time (left y-axis) and the dotted line shows the change in mass for the film only sample. The dashed trace shows the chamber RH as a function of time (right y-axis).

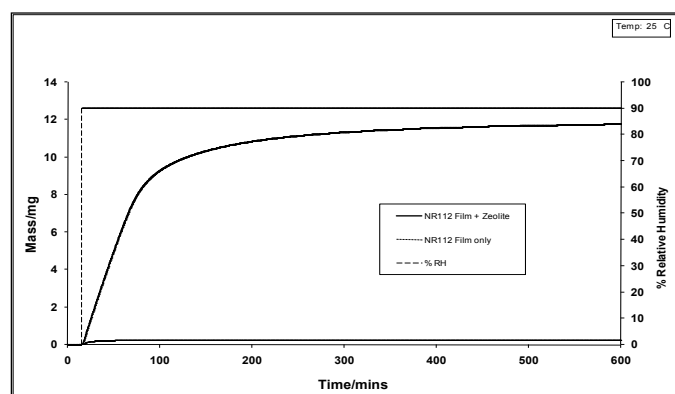


Figure 2. Moisture flux through the NR112 film at 25 °C. Film with zeolite in solid line, film only in dotted line, and RH profile in dashed line.

As outlined in the experimental section, the mass of water sorbed by the film only (dotted line in Figure 2) was subtracted from the mass uptake of the film and zeolite (solid line in Figure 2). The resulting mass change isolated the mass of water that diffused through the film and was sorbed by the zeolite. This resulting mass change was used to calculate the moisture flux. Figure 3 shows the net mass change for the NR112 sample at 25 °C. Time is normalized such that 0 minutes is the point at which the humidity is increased to 90%. The net change in mass by the zeolite has three regions: non-linear range as the film is sorbing water (below 5 minutes in Figure 3); a middle, linear region where steady-state flux occurs; followed by a second non-linear range where the zeolite becomes saturated (above 45 minutes in Figure 3). The slope in the middle, linear region, results in a steady-state moisture flux through the

NR-112 film of 0.131 mg/minute. Using the exposed surface area of film and the molecular weight of water, this flux value can be converted into  $3.70 \times 10^{-3} \text{ mol/m}^2\cdot\text{s}$ .

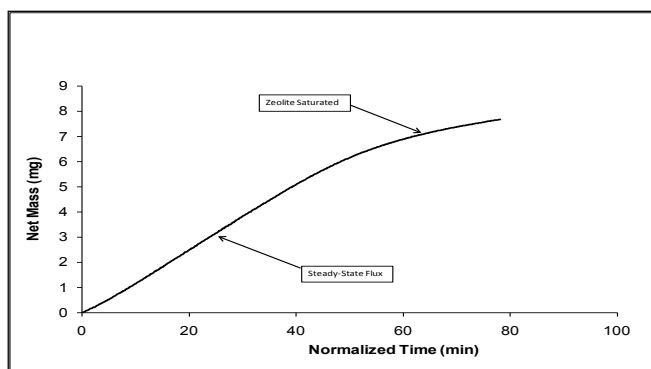


Figure 3. Net mass gain by zeolite measuring moisture flux through the NR112 film at 25 °C.

Similar experiments were performed for all three samples at 25, 40, and 60 °C. Table 1 shows the flux results in  $\text{mol/m}^2\cdot\text{s}$  for all three samples at all three temperatures. Sample thicknesses (at 50% RH, 23 °C) are also shown for comparison. Repeat experiments on the N117 sample indicate the reproducibility of these measurements is on the order of  $\pm 0.02 \times 10^{-3} \text{ mol/m}^2\cdot\text{s}$ .

Table 1. Steady-state flux values for the N-117, N-112, and NR-112 samples.

Sample	Thickness (m)	Flux ( $\text{mol/m}^2\cdot\text{s}$ )		
		25°C	40°C	60°C
N117	0.000183	1.89E-03	2.54 E-03	5.39 E-03
N112	0.000051	3.81 E-03	7.56 E-03	1.77 E-02
NR112	0.000051	3.70 E-03	7.00 E-03	1.75 E-02

Comparing the results as a function of temperature indicates the flux across the film increases with increasing temperature for all three samples. For the N117 sample the flux increases from  $1.89 \times 10^{-3}$  to  $5.39 \times 10^{-3} \text{ mol/m}^2\cdot\text{s}$  as the temperature increases from 25 to 60 °C. This is most likely due to the increased molecular mobility within the polymer at higher temperatures, which in turn facilitates water vapor diffusion through the film. Comparing the results between the N117 and N112 samples, differences in sample thickness can be investigated. At all

three temperatures, the flux values for the thinner N112 sample (51  $\mu\text{m}$ ) are significantly higher than the thicker N117 sample (183  $\mu\text{m}$ ). To illustrate, at 25 °C, moisture flux for the thicker N117 sample is  $1.89 \times 10^{-3} \text{ mol/m}^2\cdot\text{s}$ , while moisture flux for the thinner N112 sample is  $3.81 \times 10^{-3} \text{ mol/m}^2\cdot\text{s}$ . This is as expected, because the thicker sample should provide greater impedance to moisture flux through the polymer film. The differences become more pronounced at higher temperatures. At 25 °C, flux on the thinner N112 sample is 2.0 times greater than the thicker N117 sample. However, at 60 °C, flux is nearly 3.3 times greater for the N112 sample. Comparing the N112 and NR112 samples shows the effects of preparation method. For the extruded N112 sample, the flux values are slightly higher than the dispersion cast NR112 sample. The differences are greater at low temperatures. At 25 °C the difference in flux values between the N112 and NR112 samples is  $0.11 \times 10^{-3} \text{ mol/m}^2\cdot\text{s}$ , while at 60 °C the difference is only  $0.02 \times 10^{-3} \text{ mol/m}^2\cdot\text{s}$ . The latter difference is approaching the error margins of the measurements



## Conclusion

Moisture flux experiments were performed on three Nafion® based films over a range of temperatures using a novel vapor flux cell. For all three samples, flux increased with increasing temperature. Flux values measured on the thicker N-117 sample were significantly lower than for the thinner N-112 sample, most likely due to diffusion limitations. The extruded N-112 sample had a slightly higher flux values compared to the dispersion cast NR-112 sample. Future work would like to investigate flux values on a wider range of temperatures, membranes and vapors (i.e. methanol).

## Acknowledgement:

The authors thank Dr. Mark Roelofs and Mr. Dennis Curtin of DuPont Fuel Cells for providing the samples.

## References

- 
- [1] T.V. Nguyen and N. Vanderborgh, J Membrane Sci. Vol. 143, p. 235 1998.
  - [2] W-k Lee, S. Shimpalee, and J.W. Van Zee, J Electrochem. Soc. Vol. 150 p. A341 2003.
  - [3] T.A. Zawodzinski, M. Neman, L.O. Sillerud, and S. Gottesfeld, J. Phys. Chem. Vol. 95 p. 6040 1991.
  - [4] G.Q. Lu, F.Q. Liu, and C.-Y. Wang, Electrochemical and Solid-State Lett. Vol. 8, p. A1 2005.
  - [5] O. Savadogo, J. New Mater: Electrochem. Syst. Vol. 1 p. 47 1998.

Head Office:  
Surface Measurement Systems, Ltd  
5 Wharfside, Rosemont Road  
London HA0 4PE, UK  
Tel: +44 (0)20 8795 9400  
Fax: +44 (0)20 8795 9401  
Email: [science@surfacemeasurementsystems.com](mailto:science@surfacemeasurementsystems.com)

United States Office:  
Surface Measurement Systems, Ltd, NA  
2125 28<sup>th</sup> Street SW, Suite I  
Allentown PA, 18103, USA  
Tel: +1 610 798 8299  
Fax: +1 610 798 0334

